Reports from Other Journals

Research Advances

by Angela G. King

Cars of the Future—Powered by Poison?

Platinum catalysts allow low temperature proton-exchange membrane (PEM) fuel cells to obtain electricity from the combustion of hydrogen gas. But the Pt catalysts are poisoned when they are contacted by carbon monoxide, a contaminant in hydrogen gas produced from fossil fuels. Typically, fuel cells employ the water–gas shift (WGS) reaction to avoid this problem by converting the CO to CO_2. But removing the poisonous CO through the WGS reaction presents problems. First, the reaction is slow at temperatures (~500 K) where the equilibrium favors CO. Second, the WGS reaction requires large amounts of water, which makes the fuel cells too bulky to be used in portable systems.

Researchers at the University of Wisconsin–Madison's Department of Chemical and Biological Engineering have recently developed a new approach that does not require the WGS reaction and can operate at room temperature. Their system uses a polyoxometalate (POM), such as $H_3PMo_{12}O_{40}$, as an oxidant of CO and a storage site for electrons and protons. The POM is contacted with gold nanoparticles, which has the additional benefit that gold nanoparticles are known to catalyze CO oxidation in the presence of water. This new approach can be represented by the equation:

$$CO(g) + H_2O + PMo_{12}O_{40}^{3-}(aq) \rightarrow$$

$$CO_2(g) + 2H^+(aq) + PMo_{12}O_{40}^{5-}(aq)$$

Thus the carbon monoxide is removed from the gas stream and the resulting aqueous solution contains reduced metal ions that can be reoxidized at the fuel cell anode. The oxidized POMs are then returned to the reactor containing the gold nanoparticles or nanotubes, thereby starting the cycle again. In this manner the POMs are acting as a redox shuttle for electrons while eliminating the need to remove CO from the system. Protons can pass through the fuel cell's proton–exchange membrane to the cathode. Note that the reduction of the POM does not occur at room temperature without the gold catalyst. The rate of CO_2 production from this system increases with the POM concentration up to 0.05 M and follows first-order kinetics with respect to the concentration of CO in the gas stream. The rate of CO oxidation can be followed by UV–vis spectroscopy, since the POM changes from yellow to deep blue when reduced.

This system is ideal for producing hydrogen from biomass-generated hydrocarbons that generate H_2 and CO in nearly equal amounts during catalytic decomposition. The new process opens the door to utilizing renewable energy sources, such as agricultural waste, and has gathered interest from industry.

More Information

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2. Service, R. Fuel Cell Draws Power from Poison. *Science* **2004**, *305*, 1225.
3. Online descriptions of fuel cell basics are available at *http://pubs.acs.org/cen/news/8232/8232notw4.html* and *http://www.eere.energy.gov/RE/hydrogen_fuel_cells.html* (accessed Jan 2005).
4. *The Hydrogen and Fuel Cell Letter* covers alternative energy news. Monthly feature stories are available without charge at *http://www.hfcletter.com/* (accessed Jan 2005).
5. A different approach to improving fuel cells was featured in an earlier Research Advances column; see *J. Chem. Educ.* **2004**, *81*, 1086.

Prehistoric Beverage Choices

Fermented beverages have been consumed throughout the world and throughout the ages. Popular because of ethanol's analgesic, mind-altering, and disinfectant effects, fermented drinks also afford food and beverages increased nutritional value and longer shelf life. The desire for beverages based on fermented sugar has historically driven societies' agriculture, food processing, and horticulture developments.

In China, celebrations and rituals involving fermented beverages are well documented. Oracle transcriptions from the Shang Dynasty (1200–1046 B.C.E.) note at least three fermented beverages. *Chang* was an herbal wine while *li* was a sweet rice or millet beverage of low alcohol content. *Jiu* was a beverage also based on fermented rice or millet but it was filtered, producing a wine, and had an alcohol content of approximately 10–15% by mass, higher than that of *li*. Two additional fermented beverages were recorded during the Zhou period (1046–221 B.C.E.): *luo*, which was made from fruit, and *lao*, an unfiltered fermented rice or millet beverage.

Based on the similarities between Neolithic pottery vessels and vessels used to serve, store, and drink alcoholic beverages during the Shang dynasty, historians have postulated an undocumented use of fermented beverages in China in even earlier periods. Now scientists have employed an interdisciplinary approach (chemistry, archaeobotany, and archaeology) that provides evidence for fermented beverage production in China as early as 7000 B.C.E. The researchers have also documented the development of specialized saccharification fermentation system during a 5000-year period.

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Figure 1. Typical jars with high flaring necks and rims, which were well-suited for serving a fermented beverage. From Jiahu, Henan province, China, ca. 7000–6600 B.C.E. Patrick E. McGovern and his colleagues analyzed similar jar shards and discovered that they contained a mixed fermented beverage of rice, honey, and fruit (hawthorn fruit and/or grape). Photo courtesy of Zhiqing Zhang and Juzhong Zhang, Institute of Cultural Relics and Archaeology of Henan Province, Zhengzhou, China.

Figure 2. This lidded wine jar *(you)* was one of more than 90 bronze vessels associated with an elite burial in the Changzikou Tomb (Luyi county, Henan province). 52 lidded examples, including this one, were still a quarter- to half-full of liquid when the tomb was opened. Chemical isotopic analyses indicate the vessels held either *jiu* or *chang*. The rice wine in the vessel would have been made by saccharifying the grain sugars with molds, a uniquely Chinese contribution to fermented beverage making. Photograph courtesy of Zhiqing Zhang, Institute of Cultural Relics and Archaeology of Henan Province, Zhengzhou, China.

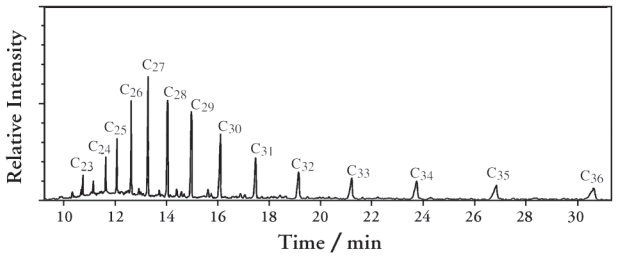

Figure 3. GC–MS analysis of chloroform extract of a Neolithic storage vessel from Jiahu (see Figure 1) showing a series of *n*-alkanes. Copyright 2004 National Academy of Sciences.

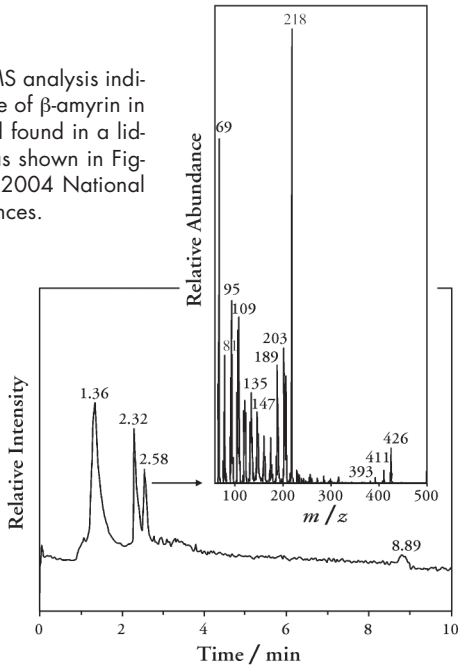

Figure 4. HPLC–MS analysis indicates the presence of β-amyrin in the Anyang liquid found in a lidded vessel such as shown in Figure 3. Copyright 2004 National Academy of Sciences.

Pottery vessels from Jiahu, a Neolithic Chinese village, were radiocarbon-dated (to 7000–5500 B.C.E.), extracted, and analyzed. The pottery included jars with high flaring rims (Figure 1) and two-handled narrow-mouthed jars ideal for preparing, serving, and storing fermented beverages. In addition, liquids found in two bronze vessels from the Shang dynasty were analyzed. The liquid-containing vessels included a lidded *he* "teapot" and a lidded *you* jar (Figure 2) from elite burial sites. Chemical constituents of the extracts and liquids were identified through a combination of GC–MS, HPLC–MS, FT–IR, stable isotope analysis, and selective Feigl spot tests for tartaric and oxalic acids (see Figures 3 and 4).

The extracts from 13 of 16 Jiahu samples were markedly similar in their analytical profiles and closely matched FT–IR and HPLC and UV profiles of modern rice and rice wine, grape wine, and modern beeswax and herbal constituents. The most straightforward interpretation of data is that the Jiahu vessels contain a fermented beverage made from rice (the only grain recovered through work at Jiahu), honey, and a fruit. Beeswax is almost impossible to completely filter out when working with honey, and unlike the sugars in honey, it does not rapidly degrade. The presence of beeswax in the vessels was supported by a homologous *n*-alkane series detected by IR and HPLC matches. Tartaric acid was identi-

fied in the Jiahu extracts and the leading candidate for its source is the Chinese hawthorn. This fruit has four times as much tartaric acid as grapes and a high sugar content that could harbor yeast. In addition, its seeds were identified by archaeobotanists working at the Jiahu site. Grape seeds were also recovered.

The liquid samples from the lidded bronze vessels showed a marked difference from the Jiahu extracts. No beeswax was detected, ruling out the use of honey. The major grain component was most likely millet, as indicated by a stable isotope determination. In addition to benzaldehyde and acetic acid, commonly found in grape wines, thermal desorption GC–MS identified camphor and α-cedrene in the liquids. The most likely source(s) of these compounds are specific tree resins, flowers, or aromatic compounds, leading to the conclusion that the vessels contain either *jiu* or *chang*.

Applications of analytic methods have ended the speculation that fermented beverages were produced in prehistoric China. The results concretely demonstrate how practices documented in the Shang dynasty developed from prehistoric practices.

More Information

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Health Benefits of Chamomile

For centuries, people who have felt sick or stressed have tried drinking chamomile tea as a medicinal cure-all. Previously chamomile has been described as having antioxidant properties with antimicrobial essential oils. Compounds such as chamazulene and flavonoids have been identified in chamomile extract, but there has never been any scientific evidence supporting its use in treating minor health problems.

Now, researchers in England have employed a metabonomic strategy to examine the health effects of chamomile. Metabonomics is the quantitative measurement of the time-related multiparametric metabolic response of living things to pathophysiological stimuli or genetic modification. Their work found new evidence that the popular herbal tea may help relieve a wide range of health ailments, including colds and menstrual cramps.

"This is one of a growing number of studies that provide evidence that commonly used natural products really do contain chemicals that may be of medicinal value," says study leader Elaine Holmes, a chemist with Imperial College London. "The healthcare industry is placing increasing emphasis on functional foods, including natural remedies, yet little work has been conducted on the long-term effects of such products on human biology."

The herbal plant used in this study was German chamomile *(Matricaria recutita),* also known as *manzanilla,* whose flowers and leaves are brewed as a fragrant, flavorful tea. The study involved 14 volunteers (seven women and seven men) who each drank five cups of the herbal tea daily for two consecutive weeks. Daily urine samples were taken and tested throughout the study, both before and after drinking chamomile tea. Researchers developed a metabo-nomic strategy that combined ^{1}H NMR spectroscopy with multivariate data analysis and orthogonal signal correction and allowed the researchers to identify subtle consequences of the varied chamomile intake.

The researchers found that drinking the tea was associated with a significant increase in urinary levels of hippurate, a breakdown product of plant-based phenolics, some of which have been associated with increased antibacterial activity. This could help explain why the tea appears to boost the immune system and fight infections associated with colds, according to the researchers. Drinking the tea also was associated with an increase in urinary levels of glycine, which has been shown to relieve muscle spasms. This may explain why the tea appears to be helpful in relieving menstrual cramps in women, probably by relaxing the uterus, say the researchers. Glycine also is known to act as a nerve relaxant, which may explain why the tea seems to act as a mild sedative; glycine supplements are sold in stores for that purpose.

Levels of both hippurate and glycine remained elevated for up to two weeks after the study participants stopped drinking the tea, indicating that the compounds may remain active for quite some time. Researchers emphasize that additional studies with larger study populations are needed before a more definitive link between the tea and its alleged health benefits can be established, but their work has validated the multivariate statistical data analysis method they used, called projection to latent structures (PLS).

More Information

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Angela G. King is Senior Lecturer in Chemistry at Wake Forest University, P.O. Box 7486, Winston-Salem, NC 27109; kingag@wfu.edu.